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engjrnal@jeng.utq.edu.iq

Effect the Dissociation of H2O and CO2 on Adiabatic Flame Temperature

Tahseen Ali Jabbar
Southern Technical University /Technical college of Basrah / Fuel and Energy Department

Abstract

In this study a theoretical model was accredited to show the effect of dissociation phenomenon on adiabatic flame temperature. CH_4, C_2H_6, C_3H_8 and C_4H_{10} as gases fuel, global reaction and a thermodynamics analysis were dependent in this model to analysis a combustion to evaluated adiabatic flame temperature. Four cases are studied no dissociation, only H_2O dissociation, only CO_2 dissociation and both H_2O and CO_2 dissociation together. The results show that with dissociation adiabatic flame temperature will be decreased and the bigger effect on adiabatic flame temperature when only CO_2 dissociation. Also the effect range of equivalence ratio on dissociation phenomenon was from 0.9 to 1.1

Keyword: combustion, adiabatic flame temperature, dissociation

1. Introduction:

Combustion is one of the complex subjects that include preliminary such disciplines as physics, chemistry, thermodynamics and fluid mechanics. Combustion has a wide diversity of uses and it is used for energy's production in power plants, gas turbines and engines. The very important index in combustion is flame temperature. If it's measured at adiabatic conditions, it will be called adiabatic flame temperature. Almost it's calculated using thermodynamic analysis. There are several parameters that's effect on the value of adiabatic flame temperature such as type of fuel, initial temperature for unburned mixture, equivalence ratio …etc.

V. Maaren and et al [1] are calculated flame temperature for flat flam burner. A relation between burnt gases temperature and the measuring burner plate temperature distribution was developed to calculate flame temperature.

They show net heat transfer from gases to plate content heat loss from flame and heat gain by burnt gases. In other hand M. Lalovic and et al [2] are study the combustion conditions for two gaseous (natural gas and mixture of gases) fuels to show the effect of change of excess air ratio values, air preheating temperature and oxygen content in air on flame temperature. They show in their results that with increasing air preheating temperature, the flame temperature increasing too. C. K. Liu and et al [3] are numerically study the phenomenon of superadiabatic flame temperature, the structure of planar freely propagating premixed flames of mixtures of CH_4/air, CH_4/O_2, $C_2H_2/H_2/O_2$, C_2H_4/O_2, C_3H_8/O_2 and H_2/O_2 was computed. Their study is perhaps superadiabatic temperatures occur only in hydrocarbon flames when the equivalence ratio of the mixture is greater than a critical value, but not in hydrogen flames. L.H. Liu and J. Jiang [4] have determined an inverse analysis for the reconstruction of temperature profile in axisymmetric free flames from the knowledge of the outgoing emission and transmission radiation intensities. Their results show that the temperature profiles can be estimated accurately, even with noisy data. Law and et al [5] are a theoretically studied adiabatic flame temperature for hydrocarbon air mixture, a water – gas shift equilibrium and dissociation of H_2O and CO_2 were studied as a parameters effect on adiabatic flame temperature. They results show the peak adiabatic flame temperature was shifted to rich side. I see that more study about effect of dissociation phenomena on adiabatic flame temperature must be done, therefor in this study four case no dissociation, onlyH_2O dissociation, only CO_2 dissociation and both H_2O and CO_2 dissociation together for CH_4/ C_2H_6/

C_3H_8 and C_4H_{10} air mixture over a wide range (from 0.7 to 1.2) of equivalence ratio will be study.

2. Theory

In this research some of assumption taken as to simplify the problem, combustion occurs at a constant pressure (atmospheric pressure), the reactants and products each form ideal gases mixture, and the reaction balance for combustion one mole of fuel expressed as [6]:

$$C_xH_y + a(O_2 + 3.76\,N_2) \rightarrow bCO_2 + cCO + dH_2O + fO_2 \quad \ldots\ldots\ldots\ldots(1)$$

Where lean combustion, there is found oxygen in products, but for rich combustion a CO found in products, while in stoichiometry condition both are not found in products. To study the effect of dissociation on adiabatic flame temperature only H2O and CO2 assuming that will be dissociate in products as the two reactions below [2]:

$$H_2O \Leftrightarrow OH + \frac{1}{2}H_2 \quad \ldots\ldots\ldots(2)$$

$$CO_2 \Leftrightarrow CO + \frac{1}{2}O_2 \quad \ldots\ldots\ldots.(3)$$

The two reversible reaction above added to the reaction of oxidizer of fuel (equation 1) yield

$$C_xH_y + a(O_2 + 3.76\,N_2) \rightarrow (b-\varepsilon)CO_2 + (c+\varepsilon)CO + (d-\alpha)H_2O + \left(f + \frac{\varepsilon}{2}\right)O_2 + \alpha OH + \frac{\alpha}{2}H_2 \quad \ldots\ldots.(4)$$

Where ε and α are the amount that dissociate from CO_2 and H_2O respectively and the constants of equilibrium for the two reversible reactions can be evaluated from table below:

Table (1) the logarithm of constant equilibrium for reaction 2 and 3 [2]

T(K)	$H_2O \rightarrow OH + \frac{1}{2}H_2$	$CO_2 \rightarrow CO + \frac{1}{2}O_2$	T(K)	$H_2O \rightarrow OH + \frac{1}{2}H_2$	$CO_2 \rightarrow CO + \frac{1}{2}O_2$	T(K)	$H_2O \rightarrow OH + \frac{1}{2}H_2$	$CO_2 \rightarrow CO + \frac{1}{2}O_2$
298.15	-45.10	-45.05	1400	-6.996	-6.004	2600	-2.043	-1.194
300	-45.08	-44.74	1500	-6.280	-5.315	2700	-1.829	-0.995
400	-33.48	-32.43	1600	-5.654	-4.711	2800	-1.631	-0.813
500	-25.09	-25.03	1700	-5.102	-4.175	2900	-1.446	-0.646
600	-21.16	-20.10	1800	-4.611	-3.697	3000	-1.273	-0.491
700	-17.64	-16.57	1900	-4.172	-3.268	3100	-1.111	-0.347
800	-15.00	-13.92	2000	-3.777	-2.879	3200	-0.960	-0.208
900	-12.95	-11.86	2100	-3.419	-2.527	3300	-0.818	-0.073
1000	-11.31	-10.21	2200	-3.094	-2.207	3400	-0.684	0.062
1100	-9.922	-8.843	2300	-2.797	-1.917	3500	-0.553	0.202
1200	-8.784	-7.739	2400	-2.525	-1.652			
1300	-7.821	-6.802	2500	-2.274	-1.412			

The total number of moles present at equilibrium is depends on case of study.

For no dissociation the total mole of products calculated as:

$$Nt_1 = b + c + d + f \quad \ldots\ldots\ldots\ldots(5)$$

For only H2O dissociation, it is written as:

$$Nt = Nt_1 + 0.5\alpha \quad \ldots\ldots\ldots.(6)$$

For only CO2 dissociation, it is written as:

$$Nt = Nt_1 + 0.5\varepsilon \quad \ldots\ldots\ldots.(7)$$

For both H2O and CO2 are dissociation together, it is written as:

$$Nt = Nt_1 + 0.5(\alpha + \varepsilon) \quad \ldots\ldots\ldots..(8)$$

The partial pressure for each component, pi, may be expressed in terms of the mole fraction and the total pressure p (total pressure assuming constant and equal atmospheric pressure).

The partial pressure of species can be written as [8]:

$$p_{CO_2} = \frac{(b-\varepsilon)}{Nt} \qquad \dots\dots\dots(9)$$

$$p_{CO} = \frac{(c-\varepsilon)}{Nt} \qquad \dots\dots\dots(10)$$

$$p_{H_2O} = \frac{(d-\alpha)}{Nt} \qquad \dots\dots\dots(11)$$

$$p_{O_2} = \frac{\left(f+\frac{\varepsilon}{2}\right)}{Nt} \qquad \dots\dots\dots(12)$$

$$p_{OH} = \frac{(\alpha)}{Nt} \qquad \dots\dots\dots(13)$$

$$p_{H_2} = \frac{\left(\frac{\alpha}{2}\right)}{Nt} \qquad \dots\dots\dots(14)$$

Since the total pressure is 1 atm, the equilibrium constant, (KP1) for reaction given by equation (2) can be expressed as:

$$K_{p1} = \frac{\alpha\sqrt{\frac{\left(\frac{\alpha}{2}\right)}{Nt}}}{(d-\alpha)} \qquad \dots\dots\dots(15)$$

And the equilibrium constant, (KP2) for reaction given by equation (3) can be expressed as:

$$K_{p2} = \frac{(c-\varepsilon)\sqrt{\frac{\left(f+\frac{\varepsilon}{2}\right)}{Nt}}}{(b-\varepsilon)} \qquad \dots\dots..(16)$$

Adiabatic flame temperature:

Adiabatic flame temperature refers to the temperature that could be attained by the products of combustion when the combustion reaction is carried out in limit of adiabatic operation of combustion chamber. Limit of adiabatic operation of combustion chamber means that in the absence of work, kinetic and potential energies the energy released during combustion shall be carried by the combustion products with minimum or no heat transfer to surroundings. This is the maximum temperature which can be attained in a combustion chamber and is very useful parameter for designers. Actual temperature shall be less than adiabatic flame temperature due to heat transfer to surroundings, incomplete combustion and dissociation etc.

The adiabatic flame temperature can be determined by use of the conservation of energy principles. To illustrate the procedure, let us suppose that the combustion air and the combustion products each form ideal gas mixtures. Then, with the other assumptions stated above, the energy rate balance on per mole of fuel basis, then:

$$\sum_P n_e \overline{h_e} = \sum_R n_i \overline{h_\imath} \qquad \dots\dots\dots\dots\dots(17)$$

Where i denotes the incoming fuel and air streams and e the exiting combustion products.

But the enthalpy can be expressed as [6]:

$$\overline{h_e} = \left(\overline{h_f^o} + \Delta\bar{h}\right)_e \quad and \quad \overline{h_\imath} = \left(\overline{h_f^o} + \Delta\bar{h}\right)_i \qquad \dots\dots\dots(18)$$

Substitute in equation 12 yield:

$$\sum_P n_e\left(\overline{h_f^o} + \Delta\bar{h}\right)_e = \sum_R n_i\left(\overline{h_f^o} + \Delta\bar{h}\right)_i \qquad \dots\dots\dots(19)$$

Re-arrangement equation 14 yield:

$$\sum_P n_e\left(\Delta\bar{h}\right)_e = \sum_R n_i(\Delta\overline{h})_i + \sum_R n_i\left(\overline{h_f^o}\right)_i - \sum_P n_e\left(\overline{h_f^o}\right)_e \qquad \dots\dots\dots(20)$$

The heat of combustion can be defined as [7, 6]:

$$Q = \sum_R n_i\left(\overline{h_f^o}\right)_i - \sum_P n_e\left(\overline{h_f^o}\right)_e \qquad \dots\dots\dots(21)$$

Heat of combustion consider very important factor effect on adiabatic flame temperature, with increasing heat of combustion adiabatic flame temperature will be increased too.

And enthalpy of species i expressed as:

$$(\Delta\overline{h})_i = \int c_p dT \qquad \ldots\ldots\ldots(22)$$

Substitute equations 16 and 17 in equation 15 and integrated it from To (298K) to adiabatic condition in products side and to initial temperature for reactants side yeild :

$$\sum_P n_e \left(\int_{T_o}^{T_{adi}} c_p dT\right)_e = \sum_R n_i \left(\int_{T_o}^{T_{in}} c_p dT\right)_i + Q \qquad \ldots\ldots\ldots(23)$$

The specific heat at constant prussure for spices taken as [6]:

$$c_p = a_o + a_1 T + a_1 T^2 + a_3 T^3 \qquad \ldots\ldots\ldots(24)$$

The cofficent ao , a1, a2 and a3 are constant. The equation (18) can be solved for unknown Tadi.,(adiabatic flame temperature) by using Newton Raphson Method.

3. Results:

The phenomenon of dissoication is consideration endothermic reaction, therfor the combustion with dissociaton will be resulted to reduce in adiabatic flame temperature. This actuality was shown by Desmond E. Winterbone [7],where he was motioned the effect of dissociation is to reduce the tmperature of products after combustion. A figure (1), as cited in refrence [7] show the internal energy - temperature digram for combustion both with and without dissociation. This turn, redues the amount of energy that can be drwon from the combustion process and reduces the work output of engines. In figure (2) the adiabatic flame temperature was ploted with equivalance ratio for methan, ethan, probane and butane fuels. In this figure can be noted the adiabatic flame temperature was approximately have same values along the wide range of equivalance ratio (from 0.7 to 1.3) except at stoichomatry value there are different in its values.

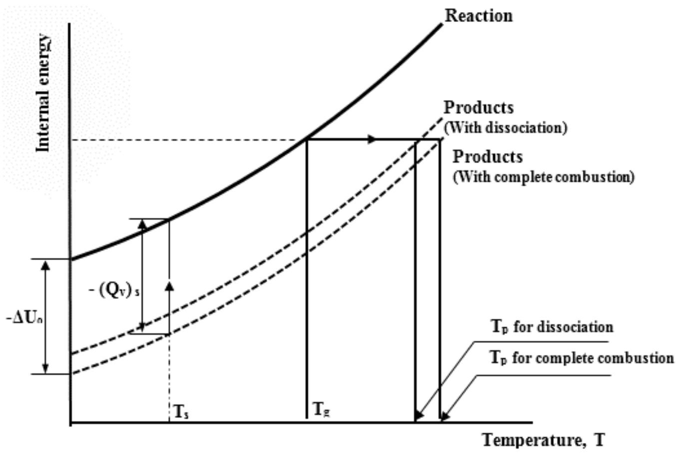


Figure (1) internal energy - temperature diagram for combustion both with and without dissociation

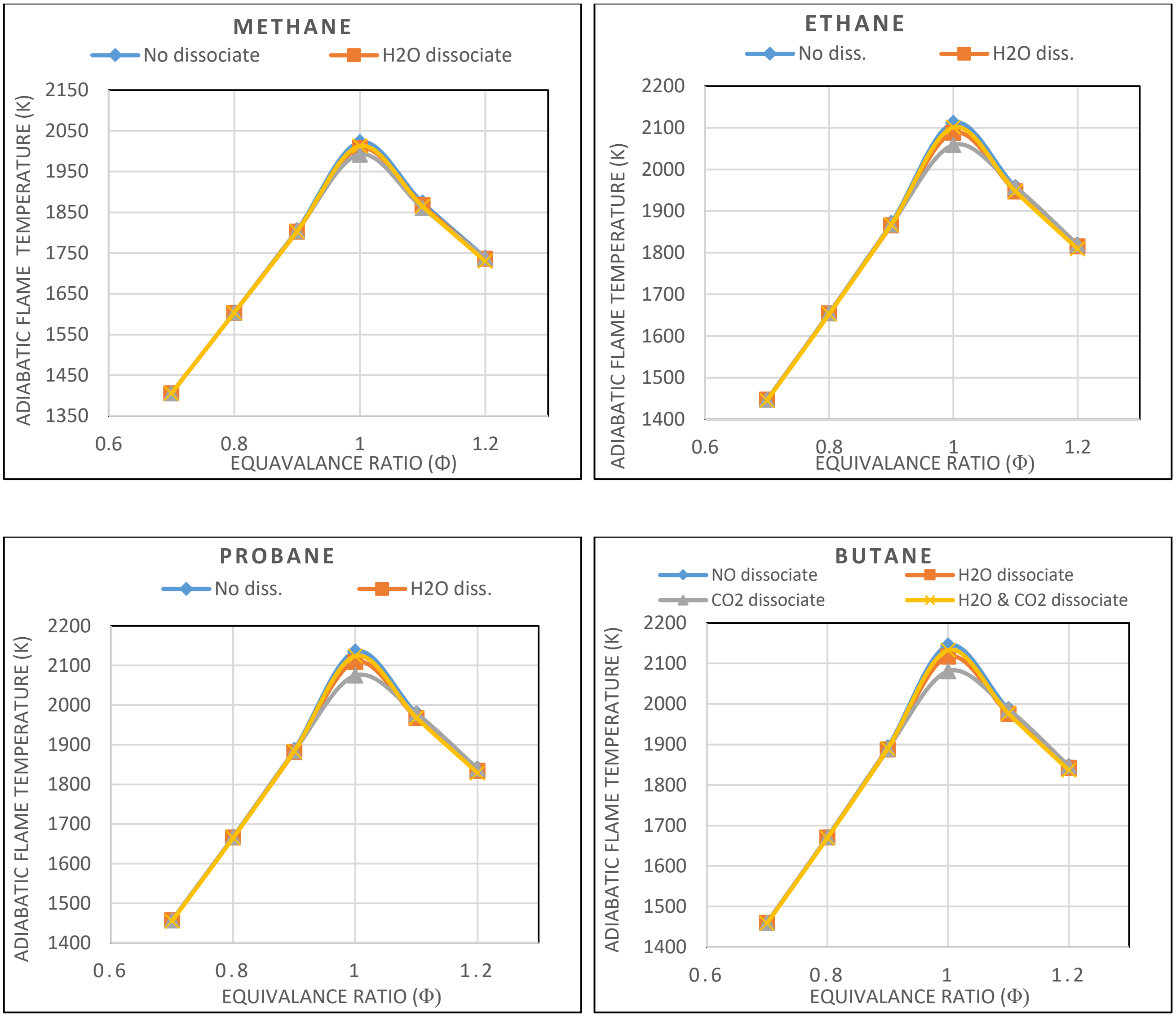


Figure (2) adiabatic flame temperature viration with equivalance ratio

The amount of dissociation is dependes on the temperature and it well be increased when temperature increasing too, due to the equilibrium constants for reversible reactions 2 and 3 are increasing at high temperature as shown in table 1. The dissociation is significant at temperature higher than 1500K as cited in refrence [8]. Therefor, in this study, the results will be taken and closed at range of equivalance ratio (from 0.9 to 1.1), at this range the adiabatic flame temperature will be higher than others range (greater than 1500K) consequence the degree of dissociation will be higher and can be see the effect of dissoication in this range as will be shown in figure (5). To show the effect heat of combustion on adiabatic flame temperature a figure (3) was ploted as a heat of combustion at same equivalance ratio (stoichometry condition Φ=1) for multi fules, where the adiabatic flame temperature was proporationed with heat of combustion as in equation 18. In figure (3), can be noted that the heat of combustion variation for methan, ethane, probane and buatane fuels with and without dissociation, the heat of combustion change with the dissociation occures. Maximum values heat of combustion occures without dissoicate for all fuels whiel the minmum values when the only CO_2 was dissociating. To understanding this phenomenon a figure (4) was ploted for methane fuel and others fuels has same behaver, where in figure (4,a) can be noted if the mole fraction of CO is increased the heat of combustion will be decreased, while invers effect of CO_2,due to some of chemical energy storage in a CO (carbon monoxide can be oxidized as fuel) then the net unchained energy (heat of combustion) in this case(the carbon dioxied dissociate) will be lass than others. Also, in this figure, the heat of combustion will be increased when the mole fractins of CO_2, H_2 and OH are increased too, but it is decreased when the mole fraction of H_2O is increased.

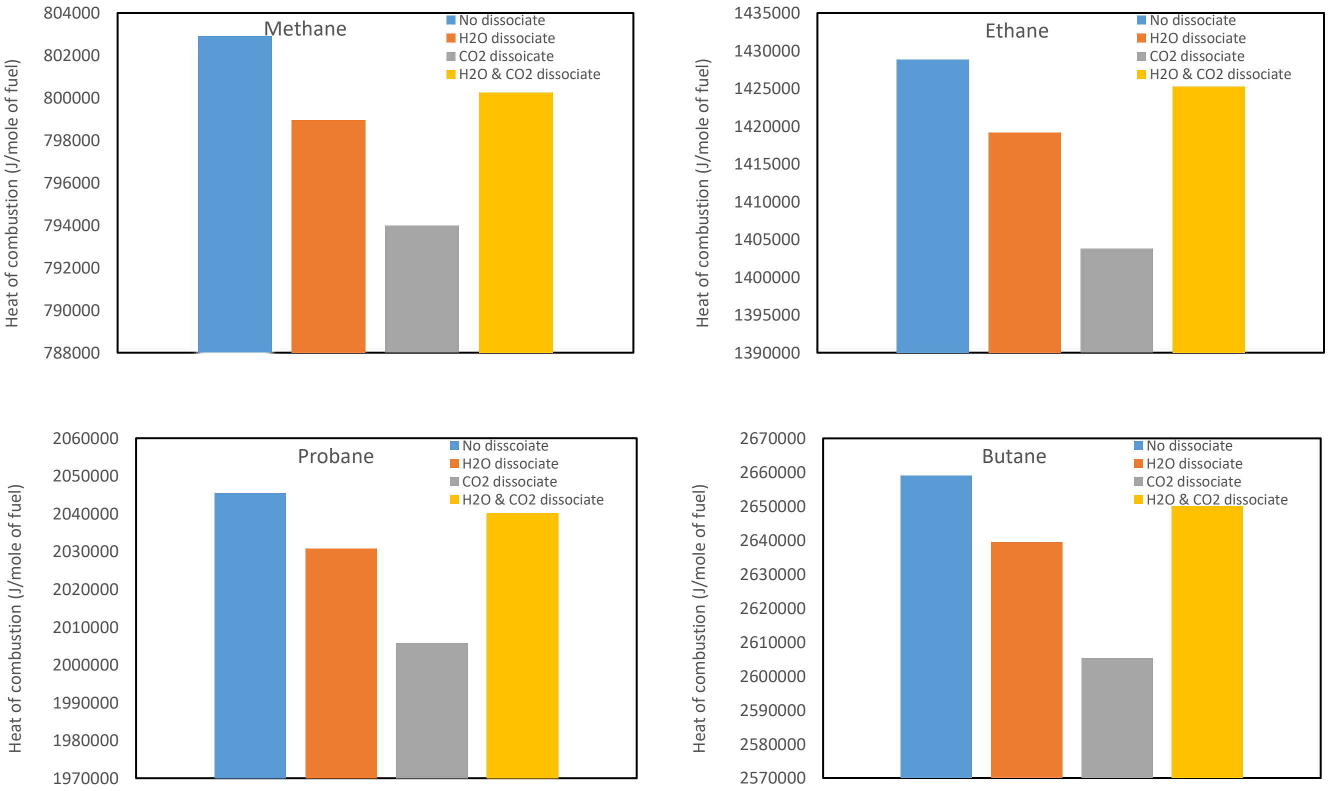
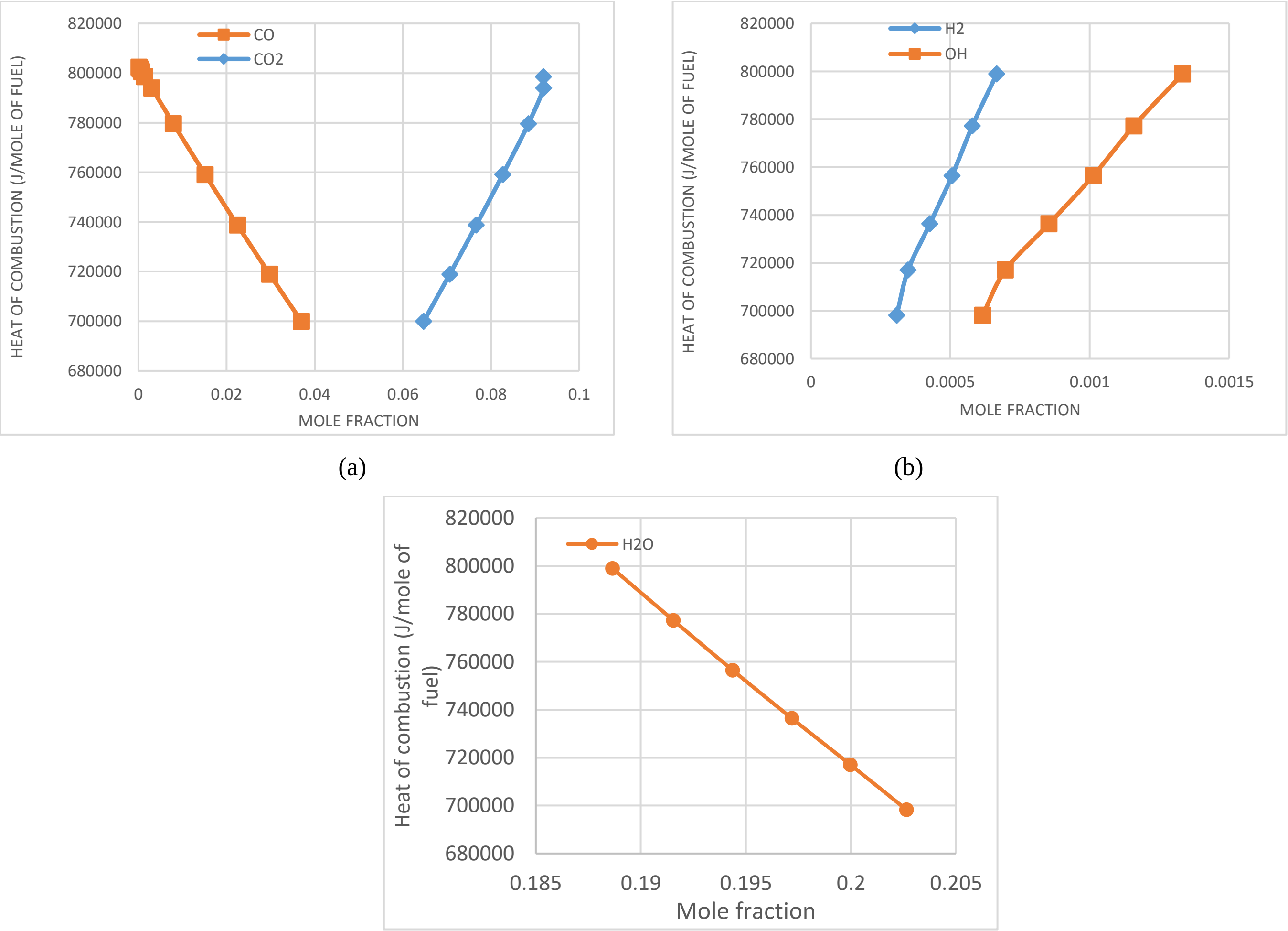


Figure (3) variation heat of combustion

In case of only H2O is dissociation, the heat of combustion is greater than when only CO2 is dissociation figure (3), this can be caused: if CO2 is dssociating then mole fraction of CO2 is decreasing that lead to heat of combustion will be dcreased too as shown in figure (4,a). Additional, when the H2O is dissociation perform to decreased the mole fraction of H2O, as shown in figure (4,c), this caused increasing in heat of combustion, therfor the heat of combustion in case of only H2O dissociation is greater than when only CO2 is dissociation. By return to figure 3, the heat of combustion, when both H2O and CO2 are dissociating, is greater than only H2O or CO2 is dissociating, that can be explains, for this case (both dissociation), dut to rducing mole fraction for H2O and CO2 together, by rducing the mole fraction of H2O lead to increasing in heat of combustion as shown in figure 2,c comparsino with only H2O or CO2 dissocisting case. While rducing in mole fraction of CO2 will be performed to decreasing in heat of combustion as shown in figure 2,a comparsion with no dissociation case. From demonstrate above can be considered amidst case between no dissociation and dissociating only H2O or CO2 case was occurred when both H2O and CO2 are dissoication together. From the results explined in figures 3 and 4 can be told the bigger adiabatic flame temperature must be considers when no dissociation occures and the smallest adiabatic flame temperature must be occurred with only CO2 was dissocating, and ralatively the adiabatic flame temperature, when both H2O and CO2 wear dissociation, was higher than only H2O or CO2 was dissociation. This actuality can be see clearly in figure (5). In this figure, for all fuels, can be shown the higher adiabatic flame temperture occures when no dissociation case and the lower adiabatic flame temperature occures when only CO2 was dissociation.



(a)

(b)

(c)

Figure (4) variation of heat combustion with mole fraction for Methane fuel

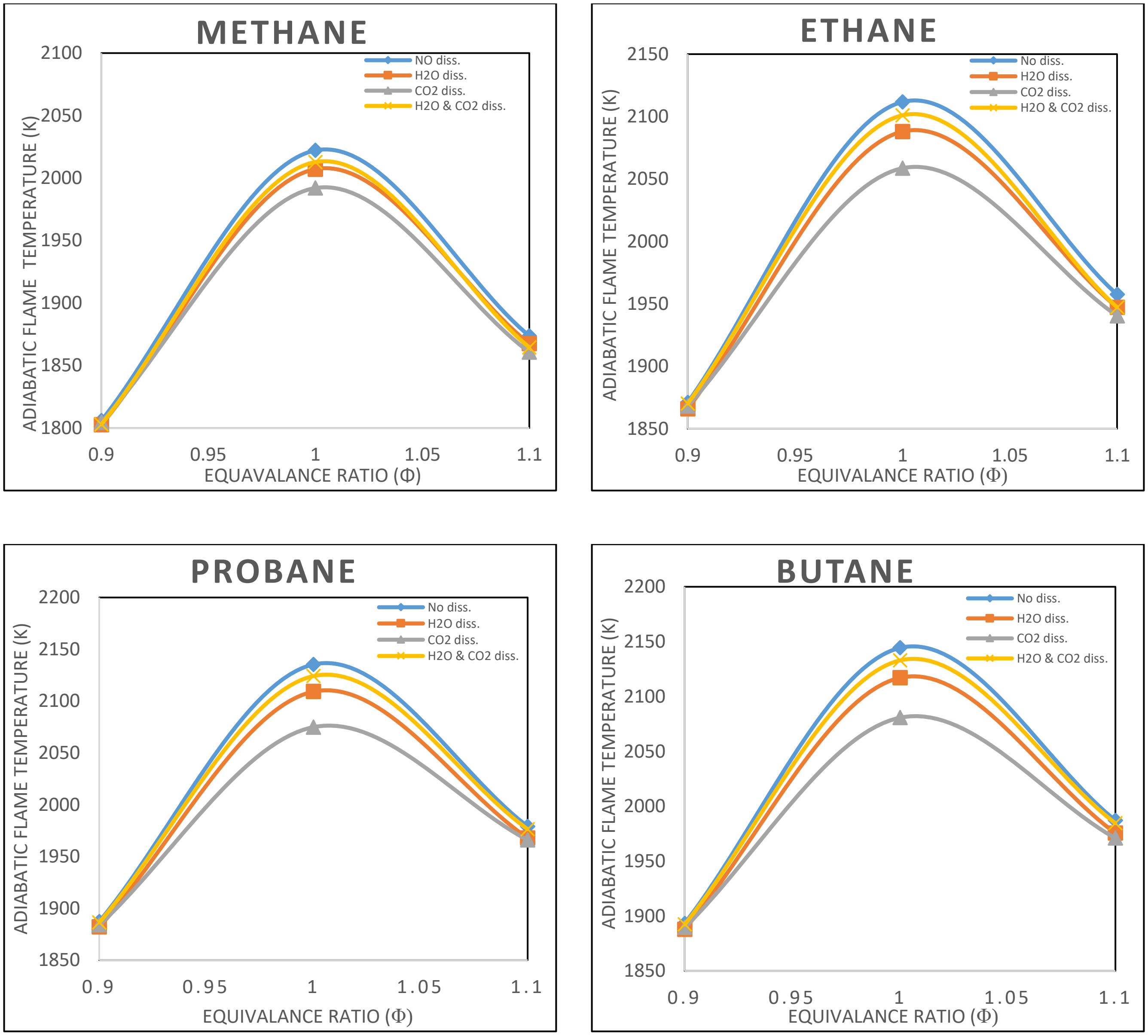


Figure (5) the effect of dissociate H2O and CO2 on adiabatic flame temperature.

Conclossion

To explore the effect of dissociation on adiabatic flame temperature a theroratical model was utilized in this study no dissociation, only H2O dissociation, only CO2 dissoication and both H2O and CO2 dissociation together. From the results shown above can be concluded the following:

With dissociation occures the adiabatic flame temperature is decreasing.

The dissoication is significant at range of equivalance ratio (0.9 to 1.1) on adiabatic flame temperature.

The CO2 has the bigger effect to reducing of adiabatic flame temperature coparative with only H2O or both H2O and CO2 dissociation.

Symbol

Symbol	Definition	SI Units
a	Number mole of air	mole

b	Number mole of CO_2 in products	=
c	Number mole of CO in products	=
cp	Specific heat at constant pressure	kJ/kg K
d	Number mole of H_2O in products	mole
f	Number mole of O_2 in products	mole
h	Enthalpy	kJ/kg K
K_p	Equilibrium constant	
n	Number mole	mole
p	Pressure	N/m^2
Q	Heat of combustion	J/mole of fuel
T	Temperature	K
Greek symbols		
α	Amount dissociate from CO_2 in products	mole
ε	Amount dissociate from H_2O in products	mole
ϕ	Equivalence ratio	
Subscribe		
adi	Adiabatic condition	
e	exiting combustion products	
i	Incoming fuel	
in	Initial	
o	Original	
P	Products	
R	Reactants	

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